Vanadium oxide thin films as the cathode in lithium micro-battery prepared by RF magnetron sputtering technology*

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Abstract: The vanadium oxide thin films prepared by RF magnetron sputtering system were investigated in an attempt to prepare amorphous vanadium pentoxide (α-V_2O_5) as the cathode film in lithium micro-battery. The film's phase and composition were characterized by X-ray diffraction (XRD) and X-ray photo spectroscopy (XPS). It is found that high-purity α-V_2O_5 thin films can be prepared by adjusting flux ratio of O_2 and Ar, substrate temperature and sputtering power. Furthermore, the electrochemical properties of α-V_2O_5 as the cathode film in lithium battery were characterized by configuring the half cell V_2O_5/$LiPF_6$/Li. After 10 discharge cycles of the cell, the discharge capacity reaches to a stable level.

Key words: α-V_2O_5; cathode film; RF sputtering; lithium micro-battery

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1 Introduction

In a thin film lithium battery, the cathode film is an important material so that the cathode material with high property has been a very popular research topic[1]. Currently, widely used materials such as $LiCoO_2$ has the theoretical capacity of 274mAh/g, which has the higher capacity than $LiNiO_2$ and $LiMn_2O_4$[1,2]. While V_2O_5 has very high capacity of Li insertion. In theory, average one vanadium atom of V_2O_5 can accept two Li atoms, which makes the V_2O_5 become a very attractive cathode film in high capacity lithium battery[3]. The capacity of Li insertion for crystalline V_2O_5 is less than 150mAh/g, while for amorphous V_2O_5 it is as high as 700mAh/g[4]. But as a metal oxide, vanadium has different valence, such as vanadium oxide can be divided into three series: VO-V_2O_3-VO_2-V_2O_5, V_nO_{2n-1} ($3<n<9$), and V_nO_{2n+1} ($3<n<6$)[5]. The combination of various vanadium oxides causes the difficulty for analysis and growth of single phase vanadium oxide.

In our work, the V_2O_5 thin film was prepared by RF magnetron sputtering system under optimized condition. XRD and XPS characterization were carried out to study the influence of processing conditions on the properties of V_2O_5 thin film. And the electrochemical property of V_2O_5 as the cathode film in the half-cell of V_2O_5/$LiPF_6$/Li was investigated.

2 Experimental

JC500-3/D sputtering system was used to deposit the V_2O_5 film on the substrate Si(111) with SiO_2 as the buffer layer. The specific conditions are shown in Table 1. Vanadium with the purity of 99.99% was used as the target. The mixture gas pressure of O_2 (99.99%) and Ar (99.99%) was 1.333Pa during sputtering with the Ar/O_2 at 1∶4. The thickness of film was measured by Dektak Ⅲ surface profiler.

Table 1 The sputtering conditions and the thickness of samples

No	Temperature (℃)	Power (W)	Thickness (nm)
1#	200	100	155.2
2#	200	150	185.3
3#	250	150	179.5
4#	250	200	200.9

After the deposition, the films were firstly characterized by XRD. Then they were submitted to XPS analysis in higher vacuum chamber ($>5\times10^{-7}$Pa). Monochromic Al Kα radiation ($h\nu$=1486.6eV) was used as the X-ray source.

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Electrochemical characterization of the V_2O_5 thin film was carried out in nonaqueous half-cells as shown in Fig 1. A lithium foil and 1mol/L $LiPF_6$ in the glove box were used as an anode and an electrolyte, respectively. The cell was tested in the voltage range of 1.5~3.5V at a constant current density of 10μA/cm^2.

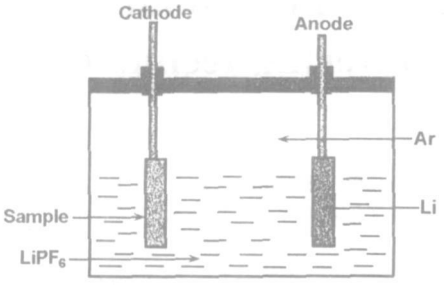

Fig 1 The configuration of half cell

3 Results and discussion

3.1 Preparation and characterization of vanadium oxide thin film

Since the valence states of vanadium are very complex, the deposited vanadium oxide thin films are multi-phase generally. The phases of the samples can be identified by XRD and XPS.

By XRD investigation, the samples show amorphous state before annealing, only a peak at 28.3° that coincides with the (111) reflection of Si The selected XRD pattern of sample 2# is shown in Fig 2. The samples show crystalline state after annealing. Fig 3 shows the XRD patterns of the samples 1#, 2#, 3#, and 4# after annealing at 450℃ for 25min in Ar. The XRD patterns of the samples all show peaks at 2θ= 20.3, 28.3, and 41.50° which coincide with the V_2O_5(001), Si(111), and V_2O_5(002) reflections. So it can be found that the samples after annealing are all V_2O_5 phase in the precision range of XRD.

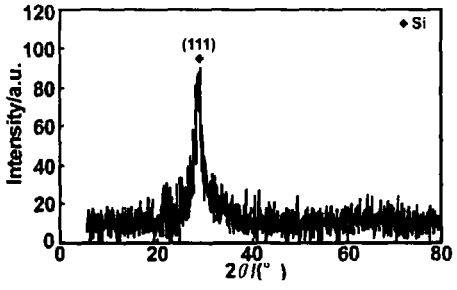

Fig 2 XRD pattern of sample 2# before annealing

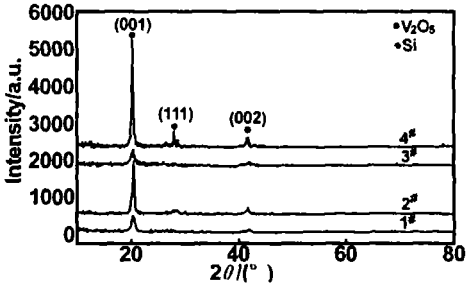

Fig 3 The XRD patterns of the samples after annealing abtained

Fig 3 exhibits that the V_2O_5 peaks in the sample 2# pattern are sharper than those in the sample 1# pattern, and the intensity ratio of (001) and (002) plane of the V_2O_5 in the sample 2# pattern is much higher than that in the sample 1# pattern. The V_2O_5 peaks of the sample 4# are sharper than those of the sample 3#, and the intensity ratio of (001) and (002) plane of the V_2O_5 in the sample 4# pattern is much higher than that in the sample 3# pattern. By comparing the sample 2# pattern with the sample 3# pattern, the same result can be obtained.

Based on Table 1 and the analysis above, it can be infered that properly decreasing substrate temperature or increasing sputtering power, better crystalline orientation with V_2O_5 after annealing can be obtained.

The vanadium oxide states of the samples before annealing are identified by XPS. Fig 4 shows the V2p and O1s XPS spectra of the samples before annealing. As shown in Fig 4, the binding energies of $V2p_{3/2}$ in the samples 1# ~ 4# spectra are respectively at 515.4, 515.3, 515.4, and 515.3eV, with the full width at half maximum (FWHM) of 3.3, 3.2, 3.3, and 3.2eV. O1s binding energies of the samples are all at 530.3eV. The energy difference between the $V2p_{3/2}$ and O1s of the samples 1# ~ 4# can be calculated as 14.9, 15.0, 14.9, and 15.0eV. According to the $V2p_{3/2}$ binding energies, FWHM of the peaks $V2p_{3/2}$ and the energy difference between the $V2p_{3/2}$ and O1s of the samples 1# ~ 4# [6], two or more vanadium oxide states should be contained in the samples.

The $V2p_{3/2}$ peaks of the samples 1# ~ 4# are all decomposed into two peaks with energy of 515.1eV and 516.7eV coinciding with the peak $V2p_{3/2}$ of V_2O_3 and the peak $V2p_{3/2}$ of VO_2. Fig 5 shows the selected sample 3#'s XPS fitting results. The contents of V^{3+} and V^{4+} can be calculated using the area of the peaks $V2p_{3/2}$ of V_2O_3 and VO_2. As shown in Table 2, the content of V^{4+} in the sample 1# is higher than that in the sample 2#; the content of V^{4+} in the sample 3# is higher than that in the sample 4#; the content of V^{4+} in the sample 3# is higher than that in the sample 2#. According to Table 1 and the analysis based on Table 2, it can be achieved that properly increasing substrate temperature or reducing sputtering power, the proportions of high valence va-

nadium oxides are increased.

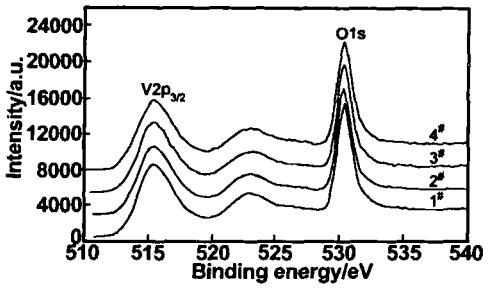

Fig 4 V2p and O1s XPS spectra of the samples before annealing

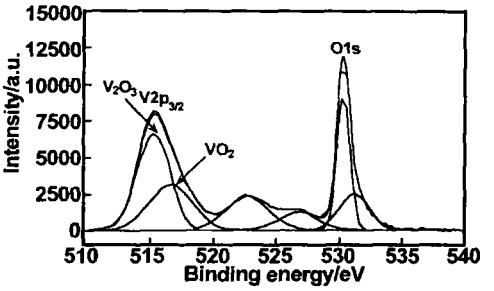

Fig 5 XPS analysis of 3# sample before annealing

3.2 Preparation and characterization of Amorphous V_2O_5 thin film

Based on the analyses above, it is found that high-purity vanadium oxide films can be prepared by adjusting flux ratio of O_2 and Ar, substrate temperature and sputtering power. High-purity α-V_2O_5 film has been prepared at the substrate temperature 250℃ with the Ar/O_2 1∶3 and sputtering power 150W. The prepared vanadium oxide film was characterized by XRD and XPS.

The XRD pattern of vanadium oxide film only shows the peak at 28.3° which is assigned to the (111) plane of Si substrate. This indicates the deposited film is amorphous. It has ever been reported that the amorphous vanadium oxide film with higher V valence state has better lithium intercalation than the crystalline vanadium oxide film with lower valence V[7]. As a result, the successful preparation of amorphous film is benefit for the performance of Lithium micro-battery.

Table 2 Fitted results of $V2p_{3/2}$ XPS for the samples before annealing

No	Valence	E $V2p_{3/2}$ (eV)	FWHM (eV)	Content (atom.%)
1#	V^{3+}	515.1	2.1	54.9
	V^{4+}	516.7	3.0	45.1
2#	V^{3+}	515.1	2.2	61.2
	V^{40}	516.7	3.2	38.8
3#	V^{3+}	515.1	2.2	53.3
	V^{4+}	516.7	3.3	46.7
4#	V^{3+}	515.1	2.2	60.5
	V^{4+}	516.7	3.1	39.5

Since the valence states of vanadium are very complex, the phase of deposited film was investigated by XPS as shown in Fig 6. The peaks due to $V2p^{3/2}$ and O1s are revealed at 517.2eV and 530.2eV respectively. The FWHM of $V2p^{3/2}$ and O1s peak are 1.4 and 1.6eV. And the distance between $V2p^{3/2}$ and O1s peak is 13.0eV. The FWHM of $V2p^{3/2}$ peak is so narrow that the combination of vanadium oxides, such as VO_2, V_2O_3 or V_2O_5, is impossible. Moreover V_2O_5 is the most stable phase of all the vanadium oxides. By considering the peak value of $V2p^{3/2}$ and the distance between $V2p^{3/2}$ and O1s peak[4], it's easy to understand that the the film is the single phase of V_2O_5.

The first discharge profile of the vanadium oxide film with the thickness 350nm is displayed in Fig 7.

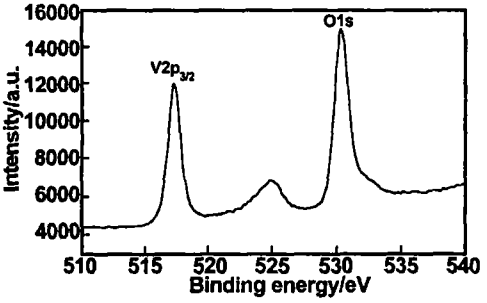

Fig 6 XPS spectrum of vanadium oxide film

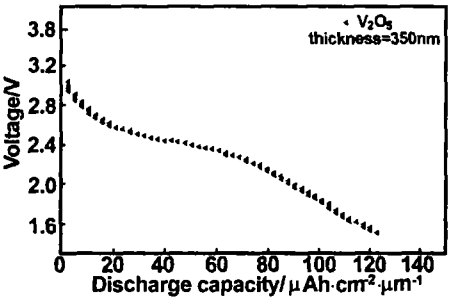

Fig 7 The first discharge curve at current desity of 10μA/cm^2 and voltage of 1.5~2.5V

The film was measured at a constant current density per volume. The discharge capacity is as high as 122μAh/cm^2 • μm and there is a stable discharge step at 2.4V. Moreover no distinguished discharge step is tested at high voltage. There is an apparent difference between the first and second discharge processing as shown in Fig 8, which reveals the cyclic property for the cell Li/$LiPF_6$/V_2O_5 at a constant current density per volume. The

second discharge capacity of the amorphous V_2O_5 film reduced to 94μAh/cm^2·μm which is less 28μAh/cm^2·μm than that in the first discharge. Then later within the first 10th discharge process, there is a quick decrease on the discharge capacity. While after 10th discharge, the loss of discharge capacity becomes slight. Even after 50th discharge, the capacity is still high at 67μAh/cm^{2}μm.

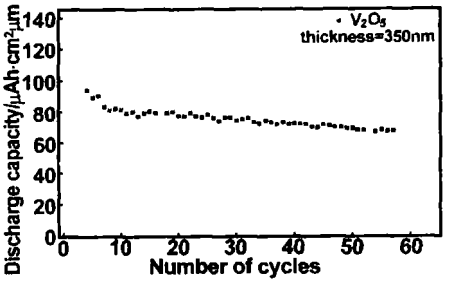

Fig 8 Cyclic property of amorphous V_2O_5 at current desity of 10μA/cm^2 and voltage of 1.5 ~ 3.5V

It can be understood that when the Li^+ inserted into amorphous V_2O_5 film at the first time, part of Li^+ will react with the amorphous film unrecoverable, which cause the big loss of discharge capacity. Then during later cycles there are Li^+ reacting with the rest active part of amorphous V_2O_5 film so that there is a quick decreasing on discharge capacity. But after ten cycles, the combination becomes saturated and the discharge capacity also reaches to a stable level. Meantime, the insertion and dis-insertion of Li^+ in amorphous V_2O_5 film may cause some damage on the film, which is a possible reason for the loss of discharge capacity.

4 Conclusion

In this work, the Vanadium oxide thin film samples prepared on SiO_2/Si(111) by R.F. magnetron sputtering have been investigated by XRD and XPS before and after annealing. XRD results demonstrate that the samples show amorphous state before annealing and crystalline state after annealing. XPS analyses exhibit that properly increasing substrate temperature or reducing sputtering power, the proportions of high valence vanadium are increased. It can be concluded that high-purity amorphous V_2O_5 films can be prepared by adjusting flux ratio of O_2 and Ar, substrate temperature and sputtering power. The electrochemical properties of amorphous V_2O_5 film as the cathode film in the half cell V_2O_5/$LiPF_6$/Li was characterized. It has been shown that amorphous V_2O_5 film has high discharge capacity even after 50th discharge.

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氧化钒薄膜作为锂离子微电池阴极膜的磁控溅射技术的制备

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摘 要: 研究了用磁控溅射系统来制备氧化钒薄膜, 通过优化工艺条件制备出可用作锂离子微电池阴极膜的非晶态五氧化二钒(α-V_2O_5)薄膜。并使用 X 射线衍射(XRD)与 X 射线光电子谱(XPS)来表征薄膜的晶向及化学组分。结果表明通过调节氧气以及氩气的流量、基片的温度和溅射功率, 可以制备出高纯度的 α-V_2O_5 薄膜。而且, 半电池体系 V_2O_5/$LiPF_6$/Li 被构造用于表征在锂电池中作为阴极膜的五氧化二钒(α-V_2O_5)的电学性质。在此电池系统经过 10 个循环放电后, 薄膜放电电容趋于稳定值。

关键词: α-V_2O_5; 阴极膜; 射频磁控溅射; 锂离子电池